Structure of Tris(*p*-fluorophenyl)triphosphorus Trisulphide

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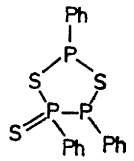
Summary The structure of the title compound is based on a five-membered ring containing a P–P bond, not on a six-membered ring as previously supposed.

TRIPHENYLTRIPHOSPHORUS TRISULPHIDE, $Ph_3P_3S_3$, occupies a key position in organophosphorus–sulphur chemistry, being easily converted by sulphur addition[1] or sulphur abstraction[2] into $Ph_2P_2S_4$ (four-membered ring)[1] or Ph_4P_4S (five-membered ring).[2,3] The originally suggested tetrameric formula[4] was later corrected;[5] among several possible structures, the most reasonable seemed to be that based on a six-membered ring of alternating phosphorus and sulphur atoms.[5] Other workers have suggested that the molecule contains a P_3 ring, the sulphur atoms being bound exocyclically.[6] We have now prepared the analogous $(p\text{-}FC_6H_4)_3P_3S_3$, whose higher solubility makes it easier to study. Its ^{19}F n.m.r. spectrum consists of three distinct multiplets of equal area, at −3·2, −3·7, and −6·9 p.p.m. relative to internal fluorobenzene, indicating three inequivalent fluorophenyl groups. The ^{31}P spectrum is of the ABX type, δ_A −36·8, δ_B −24·2, and δ_X +45·7 p.p.m. relative to external P_4O_6, J_{AB} 245 Hz. The magnitude of J_{AB} indicates a direct P–P bond, the structure shown being confirmed by a strong i.r. band at 673 cm^{-1}, attributed to



ν(P=S). Triphenyltriphosphorus trisulphide itself has a similar band at 648 cm^{-1}, and evidently has the same skeletal structure. The P_3S_3 unit is identical to one of the rings in P_4S_5,[7] and the basic $(P_2)(SPS)$ ring is also found in P_4S_3,[8] P_4S_7,[9] and both forms of $P_4S_3I_2$.[10]

We are grateful to the National Research Council of Canada for financial support and for an N.R.C. Scholarship (to M.R.L.).

(*Received, 15th October* 1974; *Com.* 1283.)

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